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# Division of Synthetic Chemistry

## – Structural Organic Chemistry –

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## Scope of Research

Fundamental studies are being conducted for the creation of new functional  $\pi$ -systems with novel structures and properties, and for evaluation of their application as organic semiconducting materials for photovoltaic and electroluminescent devices. The major subjects are: 1) organochemical transformation of fullerenes  $C_{60}$  and  $C_{70}$ , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; 2) generation of ionic fullerene species and their application for the synthesis of functional material; 3) synthesis of new carbon-rich materials by the use of transition metal complex; and 4) creation of new functional  $\pi$ -materials with unique photoelectric properties.

### KEYWORDS

$\pi$ -Conjugated Systems

Functional Materials

Radical Species

Endohedral Fullerenes

Helical Structures



## Selected Publications

Hashikawa, Y.; Yasui, H.; Kurotobi, K.; Murata, Y., Synthesis and Properties of Open-Cage Fullerene  $C_{60}$  Derivatives: Impact of the Extended  $\pi$ -Conjugation, *Mater. Chem. Front.*, **2**, 206-213 (2018).

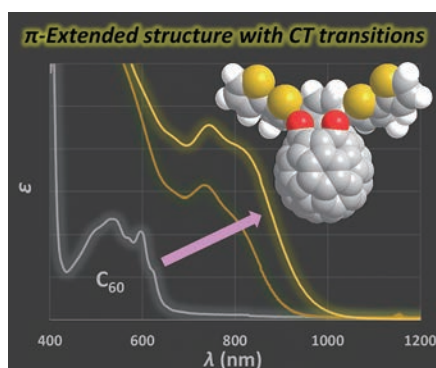
Zhu, G.-Z.; Liu, Y.; Hashikawa, Y.; Zhang, Q.-F.; Murata, Y.; Wang, L.-S., Probing the Interaction between the Encapsulated Water Molecule and the Fullerene Cages in  $H_2O@C_{60}^-$  and  $H_2O@C_{59}N^-$ , *Chem. Sci.*, **9**, 5666-5671 (2018).

Hasegawa, S.; Hashikawa, Y.; Kato, T.; Murata, Y., Construction of a Metal-Free Electron Spin System by Encapsulation of an NO Molecule Inside an Open-Cage Fullerene  $C_{60}$  Derivative, *Angew. Chem. Int. Ed.*, **57**, 12804-12808 (2018).

Strelnikov, D. V.; Jasik, J.; Gerlich, D.; Murata, M.; Murata, Y.; Komatsu, K.; Kappes, M. M.; Roithova, J., Near- and Mid-IR Gas-Phase Absorption Spectra of  $H_2@C_{60}^+-He$ , *J. Phys. Chem. A*, **122**, 8162-8166 (2018).

## Synthesis and Properties of Open-Cage Fullerene $C_{60}$ Derivatives: Impact of the Extended $\pi$ -Conjugation

We have developed the method for the synthesis of open-cage fullerene  $C_{60}$  derivatives with extended  $\pi$ -conjugation bearing thienyl groups (Figure 1). By applying this method to the unsymmetrical diketo derivative, the symmetric form can be obtained without changing the molecular formula. To investigate the structure-property relationship for the asymmetric and symmetric forms, we conducted the electrochemical and photophysical measurements. The UV-Vis absorption edge was shifted by 210 nm from asymmetric to symmetric forms due to the narrower HOMO-LUMO gap, which is also demonstrated by electrochemical analyses. From the theoretical calculations, the major contribution of the longest wavelength absorption for the symmetric form is assignable to unusual intramolecular charge transfer transitions whereas  $\pi$ - $\pi^*$  transition is dominant for the asymmetric form.

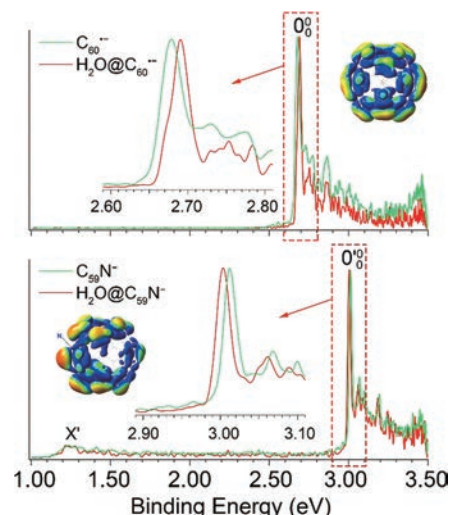


**Figure 1.** Bathochromic shift with intense absorption of open-cage  $C_{60}$  derivatives by effective  $\pi$ -extension.

## Probing the Interaction between the Encapsulated Water Molecule and the Fullerene Cages in $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$

We report a high-resolution photoelectron imaging study of cryogenically-cooled  $H_2O@C_{60}^-$  and  $H_2O@C_{59}N^-$  endohedral fullerene anions. The electron affinity (EA) of  $H_2O@C_{60}$  is measured to be  $2.6923 \pm 0.0008$  eV, which is 0.0088 eV higher than the EA of  $C_{60}$ , while the EA of  $H_2O@C_{59}N$  is measured to be  $3.0058 \text{ eV} \pm 0.0007$  eV, which is 0.0092 eV lower than the EA of  $C_{59}N$  (Figure 2). The opposite shifts are found to be due to the different electrostatic interactions between the encapsulated water molecule and the fullerene cages in the two systems. There is a net coulombic attraction between the guest and host in  $H_2O@C_{60}^-$ , but a repulsive interaction in  $H_2O@C_{59}N^-$ . We have also observed low-frequency features in the

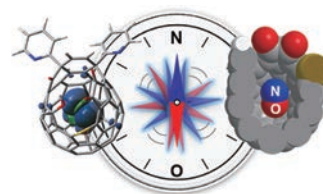
photoelectron spectra tentatively attributed to the hindered rotational excitations of the encapsulated  $H_2O$  molecule, providing further insights into the guest–host interactions in  $H_2O@C_{60}^-$  and  $H_2O@C_{59}N^-$ .



**Figure 2.** Photoelectron spectra of  $C_{60}^-$ ,  $H_2O@C_{60}^-$ ,  $C_{59}N^-$ , and  $H_2O@C_{59}N^-$ .

## Construction of a Metal-Free Electron Spin System by Encapsulation of an NO Molecule inside an Open-Cage Fullerene $C_{60}$ Derivative

A reactive radical species, nitric oxide (NO), was encapsulated as a unimolecular form inside an open-cage fullerene derivative under high-pressure conditions in solid state (Figure 3). Surprisingly, the molecular complex showed sharp  $^1H$  NMR signals in spite of the existence of the paramagnetic species inside the carbon cage. Owing to the paramagnetic shifts, the escape rate of the NO was determined experimentally and compared with the DFT calculations. After constructing a stopper on the rim of the opening to prevent such escape, the NO was found to stay inside the cage even at 50°C. The ESR measurements of the powdery sample showed paramagnetic properties at low temperature. The single crystal X-ray structure analysis clearly demonstrated the existence of the encapsulated NO molecule, suggesting rapid rotation inside the cage. The  $^1H$  NMR chemical shifts of the sharp signals displayed large temperature dependence owing to the paramagnetic effects.



**Figure 3.** Spin density map and the cross sectional image of  $NO@open-C_{60}^-$ .